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Spatial and seasonal variability of dissolved organic matter in the Cariaco Basin

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[1] Dissolved organic carbon (DOC), nitrogen (DON), and phosphorus (DOP) were measured monthly at the CARIACO Time Series station (10°30′N, 64°40′W) in the southeastern Caribbean Sea between 2005 and 2012. Marked seasonal variability in DOC concentrations was observed, with lower values (~66 μ*M*) in the upper water column (<75 m) during the upwelling season (December–April) due to the injection of cool, DOC-impoverished Subtropical Underwater from the Caribbean Sea. During the rainy season (May–November) waters were stratified and upper layer DOC concentrations increased to ~71 μ*M*. Interannual variability in surface (1 m) concentrations of DOC was also observed in response to the variable strength in upwelling and stratification that the Cariaco Basin experienced. DON and DOP showed no such seasonality. At depths >350 m, DOC concentrations were 56 ± 4.7 μ*M*, roughly 10 μ*M* higher than those in the Caribbean Sea over the same depth range. DON and DOP showed similar vertical profiles to that of DOC, with higher concentrations (6.8 ± 1.2 μ*M* N and 0.15 ± 0.09 μ*M* P) in the upper water column and invariant, lower concentrations at depth (4.8 ± 1.6 μ*M* N and 0.10 ± 0.08 μ*M* P). Wind-driven advection of surface DOC out of the Cariaco Basin was estimated to support a net export ~15 Gmol C yr^{-1} into the Caribbean Sea; this rate is comparable to the flux of settling particulate organic carbon to depths >275 m within the basin.

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1. Introduction

[2] The marine dissolved organic matter (DOM) pool is one of the largest reservoirs of reduced carbon in the ocean (~662 Pmol C) [*Hansell et al*., 2009]. Thus, small changes in the cycling of DOM can have dramatic impacts on the magnitude of CO_2 released or sequestered by marine systems. As a fundamental component of the marine food web, DOM is actively produced and remineralized in the ocean, released by organisms through numerous processes and assimilated as nutrient and energy sources by others. Phytoplankton release is one of the largest sources of marine DOM, either by exudation, viral lysis, grazing, sloppy feeding, or solubilization of particulate organic matter (POM) formed by cell aggregates or fecal material [*Jiao et al*., 2010; *Romera-Castillo et al*., 2010]. Remineralization by heterotrophic bacteria is the main sink of DOM, although removal of DOM has been also ascribed to photolysis in surface waters and to particle adsorption and gel formation at depth [*Coble*, 2007; *Hansell et al*., 2009; *Burd et al.*, 2010; *Carlson et al*., 2010].

[3] Relatively little is known regarding the composition of DOM [*Benner*, 2002]. As such, DOM fractions have been characterized according to their reactivity [*Hansell*, 2013]. Labile DOM has a rapid turnover (hours to days) and constitutes a relatively small fraction of the ocean inventory [*Hansell et al*., 2009]. Semilabile and semirefractory DOM fractions are more biologically resistant and can accumulate in the surface ocean; they cycle on the order of months to decades and account for most of the DOM that is exported from the euphotic zone to the deep ocean [*Hansell et al*., 2009; *Hansell*, 2013; *Jiao et al*., 2010]. Refractory DOM is the largest and least reactive pool of DOM in the ocean, having a mean age of 4000–6000 years [*Bauer et al*., 1992], with assumed cycling over millennial time scales [*Hansell et al*., 2009, 2012; *Hansell*, 2013].

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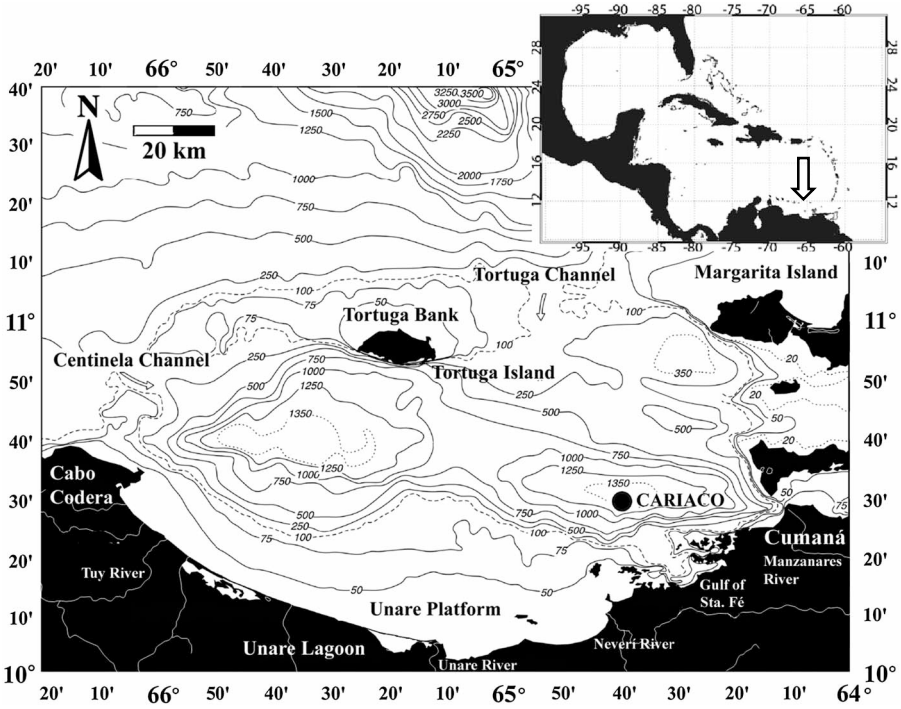

Figure 1. The Cariaco Basin. The location of the CARIACO Ocean Time Series site is indicated.

[4] DOM is a fundamental component of the microbial loop and constitutes a supply of organic matter to the deep ocean [*Hansell and Carlson*, 2001b; *Hopkinson et al*., 2002; *Jiao et al*., 2010]. It is estimated that dissolved organic carbon (DOC) export to depths greater than 100 m may account for 20% of the global organic carbon flux [*Hansell*, 2002; *Hansell et al*., 2012]. In tropical regions, DOC concentrations are highest in the upper ocean due to photosynthetically driven production and vertical stratification, which leads to the accumulation of DOM when microbial assimilation lags behind production [*Hansell*, 2002]. Tropical continental margins are areas of high spatial and temporal heterogeneity of DOM, largely controlled by the interaction between terrestrial and marine inputs.

[5] Although continental margins account for over 60% (>0.62 Pg C yr^{-1}) of the total organic carbon export to the seafloor [*Muller-Karger et al*., 2005], very little is still known about variations of DOM in these regions. Here we present a 7 year time series of seasonal DOM observations in the Cariaco Basin, a tectonic pull-apart basin on the continental margin of the southern Caribbean Sea. High primary production rates coupled with bathymetrically restricted circulation in the Cariaco Basin result in anoxia below ~250 m. These oxygen-depleted waters are home to a vast diversity of prokaryotes, protozoans, and viruses [*Taylor et al*., 2003, 2006; *Madrid et al*. 2001; *Edgcomb et al*. 2011]. Maximum abundances of these microorganisms are usually observed in the oxic-anoxic transitional zone, thus representing a complex microaerophilic/anaerobic microbial food web. Upward flux of reductants and downward movement of oxidants establish a redoxcline between ~250 and 450 m, sometimes including a sharp O_2/H_2S interface and other times a suboxic zone (undetectable O_2 and H_2S) as broad as 80 m [*Scranton et al*., 2006]. Once depleted of oxygen, concentrations of hydrogen sulfide, methane, and ammonia increase with depth, while microbial activities and abundances decrease below ~400 m [*Taylor et al*., 2001; *Scranton et al*., 2006].

2. Methods

2.1. Study Area

[6] The Cariaco Basin (Figure 1), located off the continental shelf of Venezuela, consists of two ~1400 m deep depressions that are connected to the Caribbean Sea by two ~140 m deep channels, allowing for open exchange of near-surface water but restricted circulation below the sill. General hydrographic characteristics, primary production, and particle flux processes have been examined as part of the CARIACO Ocean Time Series project [*Muller-Karger et al*., 2001, 2004, 2010; *Thunell et al*., 2000; 2004; 2007]. CARIACO is an ongoing program that has occupied a ship-based oceanographic station in the eastern basin (10°30′N, 64°40′W) at least monthly since November 1995 in a continuing effort to examine biogeochemical and ecological changes at this location.

[7] The southern Caribbean Sea is characterized by a strong seasonality. From December to April of most years, seasonal intensification of the trade winds drives coastal upwelling in the region [*Rueda-Roa and Muller-Karger*, 2013]. Primary production in the Cariaco Basin is high during this period (seasonal average of ~1700 mg C m^{-2} d^{-1}) due to the upwelling of cool (~22°C), nutrient-rich Subtropical Underwater (SUW). Rains and lower winds occur in May–November (rainy season) as a result of the more northerly position of the Intertropical Convergence Zone [*Peterson and Haug*, 2006]. This leads to an increase in stratification of surface waters, warmer surface temperatures of ~29°C, and a decrease in primary production (seasonal

Table 1. Annual Mean DOC Concentrations at the CARIACO Time Series Station Between 2005 and 2012[a]

Depth	Mean DOC	SD	DOC[b]	SD	DOC[c]	SD	C:N	SD	C:P	SD	N:P	SD
1	74	7.9	71	6.4	77	7.7	12	3	987	1137	66	96
35	67	7.4	64	6.8	69	7.2	11	3	664	543	79	95
75	63	7.0	60	5.3	65	7.1	12	5	967	773	109	136
130	59	6.6	58	6.1	59	6.4	11	4	1257	2015	110	159
200	56	6.2	54	3.5	57	7.1	11	4	574	361	52	36
~250	55	5.4	55	4.5	55	5.8	11	4	473	261	72	96
350	56	5.0	55	4.7	57	5.6	11	3	763	603	81	79
750	56	6.2	56	4.5	56	6.8	13	3	527	280	57	37
1310	56	2.5	56	2.9	56	3.0	12	5	735	861	65	62

[a]Mean values for the summer (rainy) and upwelling seasons are also given. Mean molar ratios of the DOM are for the period of 2005–2007 (all seasons included). Concentrations are in μ*M*. The ~250 m samples were collected at the oxic-anoxic interface.
SD = standard deviation.
[b]Upwelling period (November–April).
[c]Rainy period (May–October).

average of ~990 mg C m^{-2} d^{-1}), among many other concurrent changes [*Richards*, 1975; *Astor et al*., 1998; *Muller-Karger et al*., 2001].

[8] Several small rivers drain onto the southern margin of the Cariaco Basin (Figure 1). The main local rivers are the Manzanares, Neverí, Unare, and Tuy. The Tuy River is the largest, with a mean discharge of 65 m^3 s^{-1} into the western Cariaco Basin [*Recursos Hídricos de Venezuela*, 2006]. The Manzanares, Neverí, and Unare Rivers discharge into the eastern basin, with a combined discharge of ~100 m^3 s^{-1} [*Recursos Hídricos de Venezuela*, 2006]. Runoff reaches maxima between August and September [*Peterson and Haug*, 2006].

2.2. Field Sampling

[9] Vertical profiles of total organic carbon (TOC), DOC, dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) concentrations were obtained at the CARIACO Ocean Time Series station on a monthly basis aboard the R/V *Hermano Ginés* of the Fundación la Salle de Ciencias Naturales de Venezuela. Water samples were collected using a conductivity-temperature-depth/rosette equipped with 8 L Niskin bottles. DOC was sampled between July 2005 and April 2012 at nine depths [1, 35, 75, 130, 200, ~250 (adjusted to the location of the oxic-anoxic interface, in this study defined as the first depth of undetectable O_2) 350, 750, and 1310 m; Table 1], and samples were gravity filtered directly from the Niskin bottles through 47 mm precombusted (450°C, 5 h) Whatman GF/F filters (0.7 μm nominal pore size) [*Dickson et al.*, 2007] The filtrate was collected directly in acid-cleaned 60 mL high-density polyethylene (HDPE) bottles, washed three times with sample water prior to filling, and frozen until analysis. TOC samples (unfiltered water) were collected from the same Niskin bottle and stored in the same manner.

[10] DON was sampled between July 2005 and September 2009 and DOP between July 2005 and September 2007. Samples were collected at higher vertical resolution than DOC (1, 7, 15, 25, 35, 55, 75, 130, 160, 200, ~230 (adjusted to the location of the oxic-anoxic interface), 250, 300, 350, 400, 450, 500, 750, and 1310 m), vacuum filtered through precombusted (450°C, 5 h) 47 mm Whatman GF/F filters (0.7 μm nominal pore size) into acid-cleaned 60 mL HDPE bottles (washed three times with the filtrate), and frozen until analysis.

[11] Dissolved inorganic nutrients (nitrate, nitrite, ammonium, and phosphate) were sampled at the same depths as DON and DOP. Samples were vacuum filtered through 0.8 μm membrane filters (Nuclepore) into acid-cleaned 30 mL HDPE bottles (washed three times with the filtrate) and frozen until analysis. Chlorophyll *a* (Chl*a*) samples were taken in triplicate at eight depths (1, 7, 15, 25, 35, 55, 75, and 100 m). Between 250 and 500 mL of water were collected (depending on the amount of phytoplankton biomass observed during each season) and filtered through 25 mm Whatman GF/F filters (0.7 μm pore size). Samples were frozen until analysis (within 48 h of sample collection).

2.3. DOM Sample Processing

[12] All DOM samples were processed within 6 months of collection. DOC and TOC were analyzed at the University of Miami (Rosenstiel School of Marine and Atmospheric Science) via high-temperature combustion [*Dickson et al*., 2007]. Standardization was achieved using potassium hydrogen phthalate (KHP). Deep seawater and low carbon reference waters provided by the Hansell Consensus Reference Materials Program were measured every sixth analysis to assess day-to-day and instrument-to-instrument variability. The analytical precision of the DOC measurement was ~2 μ*M*. Quality control of samples was assured by comparing DOC and TOC concentrations and referencing the data against the mean of the DOC observations made at the CARIACO Ocean Time Series site at each standard depth; samples falling outside one standard deviation from the mean were excluded from our analyses.

[13] DON and DOP were analyzed at the Oceanic Nutrient Laboratory, University of South Florida. Concentrations were calculated as the difference between total dissolved nitrogen (TDN) and phosphorus (TDP) and dissolved inorganic nitrogen ($DIN = NO_3^- + NO_2^- + NH_4^+$) and soluble reactive phosphorus (SRP; HPO_4^{2-}), respectively. TDN was analyzed by persulfate oxidation [*Valderrama*, 1981]. The accuracy of the method was checked by oxidation of ammonium + nitrite standards, giving 99.5% recovery of the expected TDN concentrations and precision of 0.2 μ*M*. TDP was determined by UV oxidation [*Armstrong et al*., 1966]; 100% yield of the UV-oxidation method was confirmed by oxidation of a standard DOP compound (β-glycerol phosphate disodium salt pentahydrate). Analytical precision was 0.02 μ*M*. DIN and SRP were analyzed using a Technicon Autoanalyzer II,

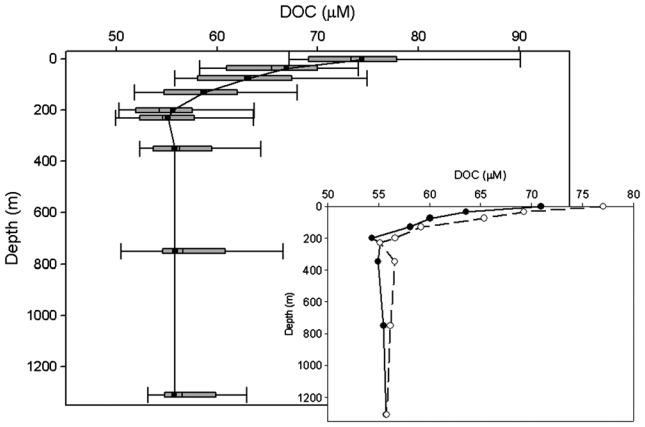

Figure 2. Box-and-whisker plot of dissolved organic carbon (DOC) at the CARIACO Time Series station. Boxes represent the interquartile (25th–75th percentiles) of all observations, the line within the box marks the median, and the rectangle within the box represents the mean. Error bars indicate the 90th and 10th percentiles. Seasonal difference in DOC concentration is shown in the inset; open circles and dashed line = rainy season; filled circles and solid line = upwelling season.

following the standard techniques described by *Strickland and Parsons* [1972], as modified by *Gordon et al*. [1993]. The precision for these measurements was within 0.5% for nitrite and nitrate, 1.3% for ammonium, and 2.0% for phosphorus. Detection limits were 0.09 μ*M* for phosphate, 0.13 μ*M* for nitrate, 0.01 μ*M* for nitrite, and 0.38 μ*M* for ammonium. Chl*a* concentrations were determined fluorometrically using a Turner Design 10-AU-005 Fluorometer [*Muller-Karger et al*., 2001].

[14] To assess spatial variability of surface DOC concentrations within the Cariaco Basin, DOC was sampled during two basin-wide cruises following the protocol described above. Thirty-five surface samples were collected during the first cruise, conducted 1–5 September 2008 (rainy season). Thirty-three samples were collected during a second cruise between 9 and 13 March 2009 (upwelling season).

2.4. Statistical Analyses and Visualization of the Data

[15] Sigmaplot V.10.0 (Systat Software, Inc.) was used to generate Figures 2 and 3. Surfer (Golden Software, Inc.), V.9.9.785, was used to generate the spatial distribution maps of Chl*a*, nitrate, temperature, and DOC. Kriging was chosen as the gridding method to produce the interpolated surfaces for Figures 4 and 5, while minimum curvature was used for

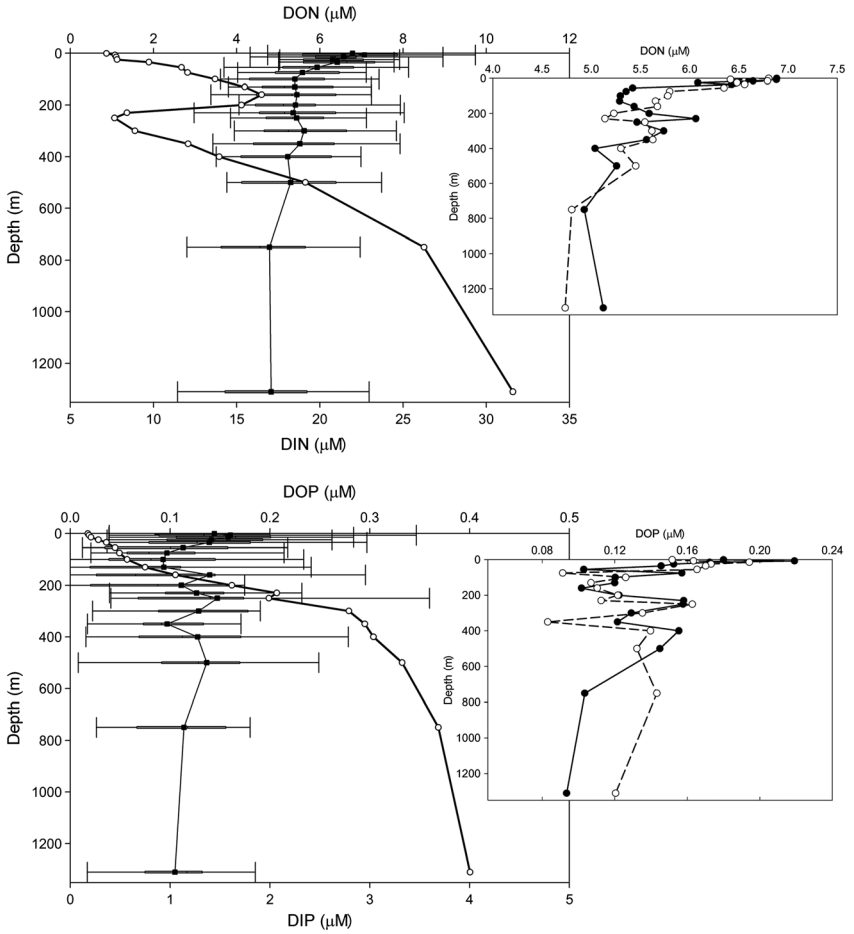

Figure 3. (top) Box-and-whisker plot of DON. DIN is also shown (solid line). (bottom) Box-and-whisker plot of DOP. DIP is also shown (solid line). Mean, median, and percentiles are as in Figure 2. Seasonal differences in DON and DOP concentrations are shown in the respective insets; symbols are as in Figure 2.

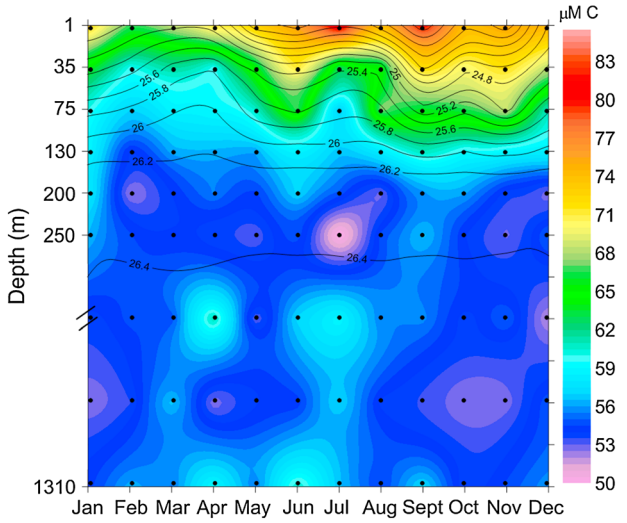

Figure 4. DOC climatology at the CARIACO Time Series station for the study period. Isopycnals are overlaid. Dots indicate actual sampling depths.

Figure 6. Welch's *t* test was used to examine whether seasonal variations in mean DOC concentrations were significantly different. A linear regression was performed to estimate the correlation between DOC concentration and temperature. All statistical calculations were performed using Microsoft Excel 2010.

2.5. Data Availability

[16] All CARIACO Ocean Time Series data are freely available in the following databases: National Oceanographic Data Center (http://www.nodc.noaa.gov/), Biological and Chemical Oceanography Data Management Office (http://osprey.bco-dmo.org/project.cfm?flag=view&id=12&sortby=project), Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/), and in the CARIACO Homepages (for English: http://www.imars.marine.usf.edu/CAR/; for Spanish: http://cariaco.ws/).

3. Results

3.1. Vertical Distribution of DOM

[17] Overall mean DOC concentrations at the CARIACO Ocean Time Series station decreased with depth in the upper 250 m, from 74 ± 7.9 µ*M* ($n = 73$) at the surface to a minimum of 56 ± 6.2 µ*M* ($n = 72$) at 250 m (Figure 2). Below 350 m, concentrations remained relatively constant, at ~56 µ*M* (Table 1). The highest DOC concentrations were confined to the upper 75 m. DON concentrations were highest in the upper 25 m, averaging 6.8 ± 1.2 µ*M* ($n = 40$; Table 2 and Figure 3). DON decreased rapidly in the euphotic zone to values of the order of 5.5 µ*M* below 100 m and reached minimum values around 4.8 ± 1.6 µ*M* ($n = 33$) at 350 m (Figure 3). DIN increased linearly from the surface to 160 m, exhibited depletions down to 250 m, and then increased to a maximum of 32 ± 1.5 µ*M* near the bottom at 1310 m (Figure 3). DON comprised over 95% of the TDN at the surface, decreasing to 12%–15% at 1310 m. DOP levels were more variable relative to mean DON values (Figure 3), with highest concentrations in the upper 25 m (0.15 ± 0.09 µ*M*; $n = 23$) decreasing to 0.10 ± 0.08 µ*M* ($n = 23$) in the anoxic portion of the water column (> 350 m). DIP increased with depth, reaching a maximum of ~4 µ*M* at 1310 m. DOP constituted ~80% of the TDP pool in surface waters (<25 m) and <3% at 1310 m (Figure 3). Temporal variability in both DON and DOP near the oxic-

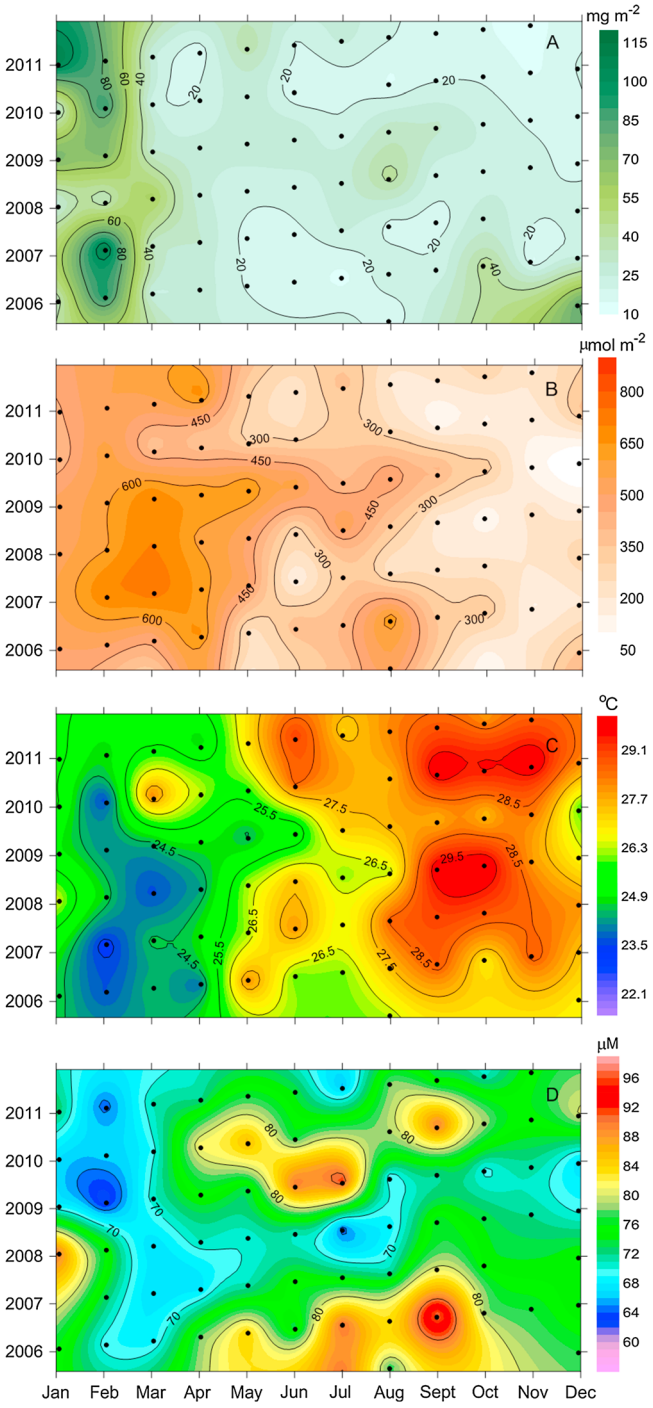

Figure 5. Climatology of (a) integrated (1–100 m) chlorophyll *a*, (b) integrated (1–100 m) nitrate, (c) surface (1 m) temperature, and (d) surface (1 m) DOC concentrations at the CARIACO Ocean Time Series site for the study period. Dots indicate actual sampling periods.

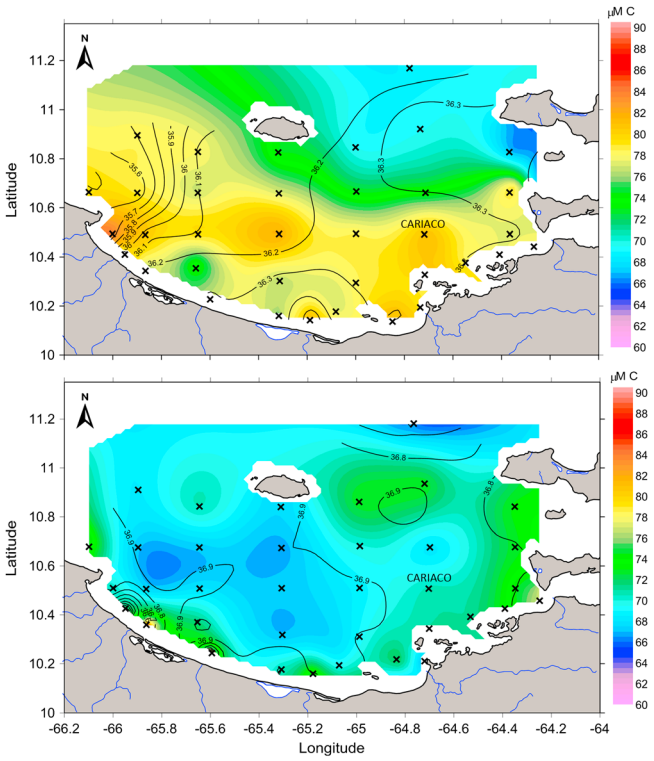

Figure 6. Distribution of dissolved organic carbon (DOC) during (top) September 2008 and (bottom) March 2009 in the Cariaco Basin. Salinity contour lines are overlaid. The location of the CARIACO Ocean Time Series site is indicated.

anoxic interface (defined as the first depth of undetectable O_2) appeared to be greater than in shallower or deeper waters, but the standard deviation was often larger than the variations observed at that depth, thus diminishing the statistical power of comparisons.

3.2. Temporal Distribution of DOM

[18] DOC exhibited significant seasonal variations ($p < 0.01$). Lower concentrations were observed in the upper 75 m during upwelling (65 ± 5.5 µ*M* C; $n = 32$) and higher (71 ± 5.9 µ*M* C; $n = 41$) during the rainy season (Table 1; Figures 2 and 4); a secondary minimum in DOC concentrations of ~7 µ*M* C was often observed during July–August. Sea surface (1 m) temperature (SST), concentrations of DOC, and integrated (0–100 m) concentrations of Chl*a* and nitrate for the study period are shown in Figure 5. Temperature was typically lowest (22°C–24°C) during the upwelling season (December–April), when integrated Chl*a* and NO_3 were highest (90–110 mg m^{-2} and 600–700 µmol m^{-2}, respectively). DOC in the upper 75 m was significantly correlated with temperature ($r^2 = 0.55$; $p < 0.01$). Neither DON nor DOP exhibited the marked seasonal changes observed in DOC, temperature, nitrate, or Chl*a* (Figure 3, insets). Temperature and concentrations of Chl*a*, nitrate, and DOC also varied interannually. For example, 2008 was a year of relatively high SST. The lowest SST was recorded in March (23.6°C), along with relatively high integrated Chl*a* (57 mg m^{-2}), nitrate (700 µmol m^{-2}), and the lowest surface DOC (67.2 µ*M* C; Figure 5). In 2008, surface DOC did not exceed 76 µ*M* C during the rainy season, while often reaching >80 µ*M* C in the rainy season of other years. Another warm year was 2011, with SST remaining above 24.6°C even during the upwelling season. DOC concentrations remained between 70 and 75 µ*M* C throughout 2011.

3.3. Spatial Distribution of Dissolved Organic Carbon

[19] Figure 6 illustrates the surface (1 m) distribution of DOC within the Cariaco Basin during September 2008 and March 2009. Overall, average DOC concentrations decreased basin-wide by ~6 µ*M* from September 2008 (~78 µ*M* C) to March 2009 (~72 µ*M* C). DOC concentrations during September 2008 were highest closer to the coast and in the western basin, where lower (~35.8) salinity water was also observed. During both September 2008 and March 2009, maximum DOC (> 80 µ*M* C) was measured near the river mouths and along the southern margin of the basin.

3.4. Elemental Ratios in DOM

[20] Mean C:N molar ratios of the DOM (July 2005 to September 2007) remained in the 10–12 range. Only minor variations were seen with depth (Table 1), and no significant seasonal variations were observed ($p > 0.01$). High variability in the DOP data introduced uncertainty in elemental ratios, such that N:P ratios ranged from 40 to 110 throughout the water column and did not vary significantly ($p > 0.05$) with season in the upper 75 m, e.g., 78 ± 15 during upwelling versus 77 ± 30 during the rainy season. C:P ranged from 470 to 1250, and there was no significant difference between seasons. C:P and N:P ratios were consistently lower near the oxic-anoxic interface.

4. Discussion

4.1. Vertical Variation of DOM

4.1.1. DOC

[21] The vertical distribution of DOC in the upper 250 m of the Cariaco Basin was similar to coastal and open ocean

Table 2. Annual Mean DON and DOP Concentrations Measured at the CARIACO Time Series Station Between 2005–2009 and 2005–2007, Respectively[a]

Depth	Mean DON	SD	Mean DOP	SD
1	6.8	1.2	0.14	0.09
7	7.1	3.2	0.16	0.12
15	6.6	1.7	0.16	0.08
25	6.3	1.2	0.14	0.07
35	6.4	1.1	0.14	0.09
55	5.9	1.5	0.11	0.10
75	5.6	1.3	0.10	0.06
100	5.4	1.5	0.09	0.08
130	5.4	1.4	0.09	0.10
160	5.4	1.4	0.14	0.25
200	5.4	1.4	0.11	0.13
~250	5.4	1.8	0.13	0.06
250	5.4	1.2	0.15	0.11
300	5.6	1.4	0.13	0.06
350	5.5	1.6	0.10	0.06
400	5.2	1.5	0.13	0.09
500	5.3	1.4	0.14	0.08
750	4.8	1.6	0.11	0.07
1310	4.8	1.6	0.10	0.05

[a]All concentrations are in µ*M*. The ~250 m samples were collected at the oxic-anoxic interface.
SD = standard deviation.

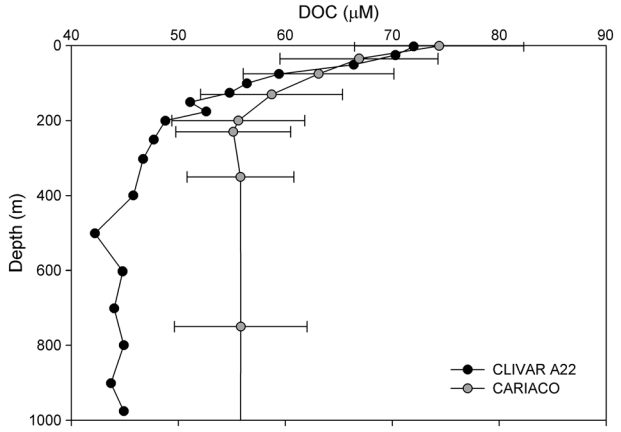

Figure 7. DOC profiles for the southeastern Caribbean Sea as obtained from station 1 from the CLIVAR A22 line (11.33°N, 64.75°W; 2003) and the 7 year average (2005–2012) at the CARIACO station. CLIVAR data taken from *Feely et al*. [2008].

regimes [*Carlson et al*., 1994; *Guo et al*., 1994, 1995; *Hansell et al*., 1997; *Hansell and Carlson*, 1998, 2001a; *Hopkinson et al*., 2002]. Deepwater DOC concentrations in the basin were ~57 μ*M*, or ~10 μ*M* higher than values at the same depths (i.e. ~300–975 m) in the Caribbean Sea (Figure 7) [*Carlson et al*., 2010]. These elevated DOC concentrations observed in deep Cariaco waters likely result from two processes. First, Cariaco Basin's deep water originates in the Caribbean Sea at depths of ~150 m [*Samodurov et al*., 2013]. A fraction of the excess DOC that is in the deep basin likely derives from this water, which has an average DOC concentration of ~52 μ*M* (Climate Variability and Predictability (CLIVAR) Repeat Hydrography, transect 22). Second, the solubilization of sinking particulate organic matter (POM) by deep microbial communities could potentially be adding DOC. Bacteria generate recalcitrant DOM as they degrade POM [*Carlson*, 2002; *Yamashita and Tanoue*, 2008; *Jiao et al*., 2010]. *Taylor et al*. [2009] found that water column anoxia in the Cariaco Basin did not significantly reduce the efficiency of bacterial POM hydrolysis, as compared to oxic waters. In addition, active viral lysis of microorganisms may also release DOC into the water column. Viral lysis of prokaryotes is a source of labile and recalcitrant DOM [*Carlson*, 2002], and viral-like particles are abundant in the anoxic waters of the basin and within sinking POM [*Taylor et al*., 2003].

[22] Some of this DOC could be a result of bacterial production. Recently, bacteria have been shown to release both labile [*Romera-Castillo et al*., 2011] and semilabile [*Jørgensen et al*., 2011] DOM, presumably as waste products of metabolism. However, in order for this DOM to accumulate in the basin's interior, utilization of DOC would have to be decoupled from its production. One explanation is that prokaryotic remineralization of DOM in the Cariaco Basin may be regulated by metabolic limitations of the microbes present, i.e., anaerobic communities cannot utilize the full array of organic substrates released by POM solubilization at their rate of production. Anaerobic metabolism is fundamentally less efficient and can utilize fewer substrates than their aerobic counterparts [*Taylor et al*., 2009]. For example, many substrates released from POM solubilization are not assimilated by fermenters or sulfate-reducing bacteria, the putative dominant ecophysiotypes in the basin's euxinic waters [*Madrid et al*., 2001]. Furthermore, *Taylor et al*. [2009] found that release and uptake of certain organic substrates were uncoupled, suggesting potential accumulation of DOM in anoxic waters. Negligible assimilation of ^{14}C-acetate, ^{3}H-leucine, ^{14}C-glucose, and other organic substrates has been repeatedly found in waters below ~450 m, suggesting slow remineralization rates [*Ho et al*., 2002; *Taylor et al*., 2001, 2006; *Taylor et al*., 2012]. The time scales of DOC remineralization in the deep Cariaco Basin are unknown. Given the short time frame of observations, it is not possible to resolve whether or not DOC has been accumulating within the deep waters. It is possible that the relatively short residence time of water in the Cariaco Basin (~100 years) [*Deuser*, 1973] may not be conducive for large DOC accumulation, such as that observed in the Black Sea (>100 μ*M* with a residence time of ~600 years) [*Ducklow et al*., 2007].

4.1.2. DON and DOP

[23] DON levels in the upper 250 m of the Cariaco Basin were similar to those measured in other marine settings [*Carlson et al*., 1994; *Guo et al*., 1994, 1995; *Hansell et al*., 1997; *Hansell and Carlson*, 1998, 2001a; *Hopkinson et al*., 2002; *Knapp et al*., 2005]. Concentrations decreased with depth from ~7 μ*M* to relatively stable values of ~5 μ*M* in deep waters. DON concentrations were lower (by ~3–10 μ*M*) than those reported by *Okuda et al*. [1969] for the Cariaco Basin during 1965 and 1967. Whether this discrepancy is due to analytical differences or natural variability cannot be determined. Deep (> 400 m) DON was comparable to Black Sea concentrations [*Ducklow et al*., 2007] but higher (by ~2 μ*M*) than western Sargasso Sea [*Hansell and Carlson*, 2001a]. While the standard deviation of observations was high, slightly elevated (0.5–1.0 μ*M*) DON concentrations were consistently observed near the oxic-anoxic interface (250–350 m), as compared to values immediately above and below this layer (Figure 3). A midwater source of labile organics has been previously proposed by *Taylor et al*. [2001]. Particle hydrolysis, trophic interactions among resident microbial populations, and bacterial production of amino acids are all processes that likely release DON within the oxic-anoxic interface [*Taylor et al*., 2009]. The proportional contribution of DON to the TDN pool in Cariaco agrees well with global averages, varying between 20% and 90% [*Bronk*, 2002].

[24] Similar to DON, DOP concentrations decreased with depth and exhibited much more variability in the oxic-anoxic interface region. This may be attributed to the release of DOP from detritus through bacterial alkaline phosphatase activity and its subsequent uptake by microbial communities [*Taylor et al*., 2009]. DOP concentrations in the deep Cariaco Basin were comparable to measurements at similar depths in oxygenated waters [*Karl et al*., 2001; *Paytan and McLaughlin*, 2007]. DOP was the dominant component of the TDP pool in surface waters (~80%); surface waters generally exhibit elevated concentrations of DOP since its main source is cell exudation and turnover [*Karl and Bjorkman*, 2002; *Paytan and McLaughlin*, 2007]. This percentage decreased to less than 3% at 1310 m, likely due to bacterial hydrolysis and diagenetic processes.

4.1.3. Elemental Ratios

[25] Elemental nutrient ratios (C:N:P) in dissolved organic matter throughout the water column showed large deviations from Redfield values (106:16:1) [*Redfield et al*., 1934]. Significant deviations from Redfield stoichiometry for both coastal and oceanic DOM have been documented [*Hopkinson et al*., 1997; *Karl et al*., 2001; *Hopkinson et al*., 2002; *Hopkinson and Vallino*, 2005], particularly in deep oceanic waters. The elemental ratios observed in the upper 75 m of the Cariaco Basin (mean = 873:84:1; Table 1) were higher than those reported for the bulk DOM pool (778:54:1) [*Hopkinson and Vallino*, 2005], particularly in the N:P ratio. This suggests that the P in DOM is recycled more efficiently than the N (or C) fractions. The lower C:P and N:P ratios within oxic-anoxic transitional waters may be due to the excess DOP released from bacterial remineralization of detrital matter, although substantial increases in DOP concentrations were not observed. Average C:N ratios did not vary significantly with depth and were in the lower end of what has been reported for DOM in the literature (~7–20) [*Carlson*, 2002; *Ogawa and Tanoue*, 2003; *Hopkinson and Vallino*, 2005; *Ducklow et al*., 2007], suggesting the presence of N-enriched DOM such as amino acids (G. T. Taylor et al., unpublished data, 2012). C:N ratios (10–12) were moderately higher than those of suspended particulate organic matter (~8) [*Benitez-Nelson et al*., 2007].

4.2. Seasonal Variation of DOM

[26] The only component of the DOM pool that exhibited a significant seasonal variation in the upper water column was DOC, with highest concentrations (71 ± 5.9 μ*M* C in the upper 75 m) observed during the rainy season. DOC variability in the surface ocean is usually controlled by biological and physical processes. Biological controls include extracellular release of DOC by phytoplankton, grazing by zooplankton, viral lysis, and decomposition by bacteria [*Daly*, 1997; *Steinberg et al*., 2000; *Carlson*, 2002; *Romera-Castillo et al*., 2010]. Physical controls involve vertical and horizontal mixing, including upwelling and wind-driven circulation [*Hansell and Carlson*, 2001a; *Álvarez–Salgado et al*., 2007]. In the Cariaco Basin surface, DOC concentrations seem to be controlled by both physical and biological drivers. During the rainy season, the Cariaco Basin experiences strong thermal stratification [*Astor et al*., 1998]. This leads to higher surface temperatures (~29°C) and nitrate depletion in the upper water column, which potentially prevent bacteria from degrading surface DOC. DIN limitation has been previously suggested as a restricting mechanism of DOM consumption by heterotrophic bacteria that leads to near-surface accumulation of DOC [*Williams*, 1995]. Thus, the ~8% higher DOC concentrations observed at the CARIACO Ocean Time Series site during the rainy season, as compared to those measured during the upwelling season, likely reflect DIN-induced limitation of bacterial DOC remineralization driven by stratification.

[27] A small decrease of 5–7 μ*M* in surface DOC concentrations during the rainy season was regularly measured during July–August. During June–July, a short and relatively weak secondary upwelling event takes place along the entire southern Caribbean Sea, linked to variations in the wind curl [*Rueda*, 2012]. This upwelled water also contains Subtropical Underwater (SUW) with less DOC (see below) which would dilute the DOC that has begun to accumulate in the surface after the cease of the primary upwelling. It is also possible that bacteria capable of degrading surface DOC are upwelled with this process [e.g., *Carlson et al*., 2004]. The DOC accumulating in surface waters after the June–July secondary upwelling likely derives from cell lysis or grazing of phytoplankton after productive periods. Similar observations of DOC accumulation in surface waters have been made in other locations that undergo seasonal thermal stratification [*Carlson et al*., 1994; *Hansell and Carlson*, 2001a; *Alvarez-Salgado et al*., 1999; *Doval et al*., 1999; *Hung et al*., 2000; *Teira et al*., 2003].

[28] Alternatively, the accumulation of DOC in surface waters could be the result of allochthonous DOC input. Allochthonous carbon sources during the rainy season in the Cariaco Basin include riverine discharge and atmospheric deposition. *Lorenzoni et al*. [2009] determined that the DOC pool in the Cariaco Basin is not significantly impacted by local river discharge on a regular basis (see also section 4.4). The atmospheric contribution of DOM has not been thoroughly quantified in this region, but initial estimates suggest that atmospheric deposition of DON is negligible compared to riverine and marine sources [*Rasse et al*., 2010].

[29] The decrease in surface DOC concentrations observed during the upwelling season likely result as surface DOC is diluted by cold, nutrient-rich, and DOC-depleted waters that emerge in the Cariaco Basin during this time. SUW has an average DOC concentration of ~57 μ*M* C [*Del Castillo*, 1998] (CLIVAR Repeat Hydrography, transect 22). Low concentrations of DOC have been observed in other upwelling systems such as the Equatorial Pacific [*Tanoue*, 1993; *Hansell and Waterhouse*, 1997] and the North Atlantic [*Carlson et al*., 2004].

[30] Upwelled water near the Gulf of Santa Fe (Figure 1), the largest upwelling focus in the Cariaco Basin, has a DOC concentration of 57 μ*M* [*Lorenzoni*, 2005]. This is located ~40 km SE of the CARIACO Time Series station. Wind-induced circulation advects the upwelled water to the northwest, past the time series site and out of the Cariaco Basin into the Caribbean Sea [*Muller-Karger et al*., 2004; *Alvera-Azcárate et al*., 2009]. The average DOC in the upper water column at the time series site during upwelling was ~10 μ*M* higher than newly upwelled SUW DOC, suggesting significant mixing with the DOC-enriched surface waters (this also includes contributions from phytoplankton and bacterial production, as well as zooplankton grazing). The outflow of this DOC-enriched water into the open Caribbean Sea results in net horizontal export of DOC from this continental margin site. The exchange of water between the Cariaco Basin and the open Caribbean is estimated to be ~0.04 Sv during upwelling [*Muller-Karger et al*., 2010]. Based on the concentrations of DOC in the SUW and the average DOC that accumulates in the upper 130 m of the Cariaco Basin during the rainy period (~68 μ*M* C; 130 m is the effective water column depth of exchange with the open Caribbean Sea) [*Alvera-Azcárate et al*., 2009], we estimated the net annual export flux of DOC to be ~15 Gmol C yr^{-1}. This carbon export is comparable to the vertical POC flux measured in the basin at 250 m (16 Gmol C yr^{-1}) [*Muller-Karger et al*., 2010] and emphasizes the importance of DOC in the carbon cycle of the Cariaco Basin. No evidence of significant vertical (via downward mixing) DOC export

was observed at the CARIACO site throughout the study period. Vertical export of DOC is limited by the strong pycnocline located between 130 and 150 m [*Scranton et al*., 1987; *Zhang and Millero*, 1993]. Select groups of fish and zooplankton migrate into the anoxic layer on a diel basis, which may influence vertical transport of particulate and dissolved organic matter within the Cariaco Basin [*Love et al*., 2004]. Indeed, downward mixing of DOC by active vertical migration of zooplankton has been suggested as a pathway of carbon export [*Steinberg et al*., 2000], but this process has yet to be quantified in the Cariaco Basin.

[31] Although high variability in measurements precludes a clear analysis, the low seasonal variability in DON and DOP in surface Cariaco Basin waters suggests that production, export by advection, and decomposition of these compounds are balanced. *Montes et al*. [2013] showed evidence of high abundance of nitrogen fixers during the rainy season in the Cariaco Basin, but the lack of variation in surface DON indicates that nitrogen fixation is not a major additional source of dissolved nitrogen to surface waters. *Thunell et al*. [2004], who examined the isotopic composition of sinking particulate nitrogen captured in sediment traps, also suggested that local nitrogen fixation was not a major source of fixed nitrogen to Cariaco surface waters. This suggestion is consistent with *Knapp et al*. [2011], who reported a lack of correlation between in situ N_2 fixation rates and DON concentrations in the subtropical North Atlantic and North Pacific over short time scales (seasonal). Other areas where no seasonal DON pattern has been observed include the Sargasso Sea (Bermuda Atlantic Time-series Study site) [*Hansell and Carlson*, 2001a] and the Santa Monica Basin [*Hansell et al*., 1993].

4.3. Interannual Variations of Surface DOM

[32] Surface DOC concentrations varied from year to year; this variation was mostly attributed to changes in upwelling intensity, which is in turn regulated by the strength and duration of upwelling-favorable winds across the eastern Cariaco Basin [*Muller-Karger et al*., 2001; *Taylor et al*., 2012]. During upwelling seasons throughout the study period, SST varied by 1°C–2°C; surface DOC concentrations varied ~4 μ*M* between years, with the highest surface DOC concentrations corresponding to those years with reduced upwelling. The direct correlation between SST and surface DOC suggests that the strength of the upwelling also regulates the amount of deep (low concentration) DOC injected into the upper water column during that season. The lower surface DOC measured during the rainy season of some years can also be related to weak upwelling. Since the source of the DOC accumulating in the surface likely derives from cell lysis or grazing of phytoplankton after the upwelling season, low productivity would lead to less available material for degradation. This was the case for 2008, where Chl*a* values were the lowest measured for the upwelling seasons of the study period (57.2 mg m^{-2}). Consequently, during the rainy season of 2008, surface DOC concentrations also remained low. Additionally, the year 2008 had a relatively strong summer upwelling (temperatures during July were 26.1°C) and deeper mixed-layer depths (MLD) (16 m during July, as compared to the 16 year average of 12 m for that same month), which likely contributed low DOC to surface waters during that time. A similar process occurred in 2011, though the months of January and February were more productive (integrated Chl*a* concentrations of ~95 mg m^{-2}); it is possible that by the time the rainy season began, most of the phytoplankton had already been degraded. The year 2011 had a relatively shallow MLD (~10 m) during its rainy season (May–November; 16 year seasonal average of 16 m).

[33] While we estimated ~15 Gmol C yr^{-1} as the average DOC export from the Cariaco Basin into the Caribbean, a year with low DOC, such as 2008, likely exported only ~10 Gmol C. A year of high DOC accumulation, such as 2006, may export upward of 19 Gmol C. Thus, interannual variability in upwelling can affect DOC export by ~30%. Note that DON and DOP concentrations did not exhibit any significant interannual change.

4.4. Spatial Distribution of Surface DOC

[34] The spatial distribution of surface DOC is defined by seasonal changes in hydrographic conditions of the basin. The overall high DOC concentrations throughout the basin measured during the rainy period of 2008, relative to the upwelling season of 2009, were in part due to surface water stratification. During stratification, DOC accumulates as a result of a breakdown of the phytoplankton bloom that occurs between December–January and April. Concentrations in the western basin during September 2008 were slightly higher (~2 μ*M* C) than those in the eastern basin, probably due to contributions from the Tuy River (close to the coast) and as a result of the circulation pattern within the basin, with inflow of higher-DOC (~78 μ*M* C) Caribbean waters through the Centinela Channel to the west [*Del Castillo*, 1998; *Hansell et al*., 2009]. While fluvial input can lead to increased DOC concentrations close to shore [*Lorenzoni et al*., 2009], the regional surface DOC distribution in the Cariaco Basin is not significantly impacted by local river discharge. The basin-wide DOC decrease from September 2008 to March 2009 was therefore caused by advection of surface water out of the basin. This process is tied to the upwelling of low DOC SUW, which dilutes the standing stock and injects DOC remineralizing bacteria into the surface waters.

[35] Little information about DOC in the Caribbean Sea exists, and it is important to stress that DOC export from the Cariaco Basin depends directly on seasonal accumulation and intensity of upwelling, which vary annually. In addition, *Alvarez-Salgado et al*. [1999, 2001, 2007] determined that upwelling filaments off Iberia and NW Africa enhance dissolved carbon exchange between the shelf and the open ocean. In particular, *Alvarez-Salgado et al*. [2007] determined that these filaments account for 2.5–4.5 times the offshore carbon exported by simple Ekman transport. The importance of this mechanism off the continental shelf of the Caribbean Sea remains unknown.

5. Summary and Future Research

[36] We present a 7 year (2005–2012) time series of DOM measurements in the Cariaco Basin, thereby providing an important contribution to the growing global ocean DOM data pool. DOM concentrations in the upper 250 m of the water column were comparable to those measured at other locations. DOC concentrations in deep (>350 m) waters were ~10 μ*M* higher than those in the adjacent Caribbean Sea at comparable depths. We attribute this difference to the source of the deep

Cariaco Basin water (Caribbean Sea water from about 150 m), as well as bacterially mediated decomposition of POC and in situ DOC production. While the large variability in DON and DOP precludes any conclusive observations, variations near the oxic-anoxic interface were likely caused by bacterial activity. However, further research is warranted on the dynamics of DOM in this particular region of the Cariaco water column.

[37] There was a significant difference in surface DOC concentrations between the upwelling and rainy seasons. During the rainy season, carbon-rich DOM accumulated in the upper 75 m of the water column due to thermal stratification of the basin. During the upwelling season, this carbon was exported through advection to the open Caribbean Sea, at an estimated 15 Gmol C yr^{-1}. The annual export of DOC from the basin is dependent on the strength of upwelling and stratification (and DOC accumulation). Interannual variability in surface DOC concentrations can result in variations on the order of 30% in the annual DOC export.

[38] This research highlights the potential importance of the microbial carbon pump as a central mechanism for the production, recycling, and consumption of DOM in the anoxic waters of the Cariaco Basin. With the expansion of oxygen minimum zones in the world's oceans linked to global climate change, the anoxic waters of the Cariaco Basin are an ideal site to observe and understand connections between anoxia, DOM cycling, and, ultimately, dissolved carbon storage.

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